Journal of Polymers and the Environment, Vol. 12, No. 3, July 2004 (© 2004)

Biodegradation Behavior of Some Vegetable Oil-based Polymers[a]

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The potential biodegradability of several vegetable oil-based polymers was assessed by respirometry in soil for 60–100 days at temperatures of 30–58°C. Films of soybean oil and linseed oil which were oxidatively polymerized (Co catalyst) on a kraft paper support were 90%–100% mineralized to CO_2 after 70 days at 30°C. Mineralization of polymerized tung oil to CO_2 was much slower than soy or linseed oils. Mineralization of epoxy resins made from epoxidized soybean oil (ESO) and aliphatic dicarboxylic acids was rapid while mineralization of similar resins made with a triacid (citric) was slower. There was no significant degradation of polyamine/ESO resins after 100 days at 58°C. Mineralization of the available carbon in vegetable oil polyurethanes and cationically polymerized ESO was less than 7.5% after 70 days at 30°C and 25 days at 55°C compared to 100% for soybean oil. From these results, it appears that triglycerides highly cross-linked with non-degradable linkages are not biodegradable to a significant extent while triglycerides cross-linked with hydrolysable bonds such as esters remain biodegradable.

KEY WORDS: Biodegradable; soybean oil; polymer; epoxidized.

INTRODUCTION

Polymerized vegetable oils such as oxidized linseed or tung oils have been used for centuries as protective coatings [1]. These oils harden on exposure to oxygen through the oxidation of double bonds to hydroperoxides followed by decomposition to free radicals and radical combination. Such "drying oils" as well as similar alkyd resins are still used today in paints, varnishes, inks and enamels.

There has been renewed interest recently in developing new polymers from soybean and other plant oils as they offer a renewable feedstock vs. finite and unreliable petroleum sources [2]. Wool et al. [3, 4] have developed a family of chemically modified oils which can be polymerized using free radical initiators into rigid composites, rubbers and adhesives. Larock et al. [5] have copolymerized native vegetable oils with synthetic monomers such as divinylbenzene using a cationic initiator such as BF_3. Petrovic et al. [6, 7] have recently developed methods for preparing soy polyols from epoxidized soybean oil and for further reacting these with diisocyanates to form polyurethanes. Such materials have applications as rigid materials or as foams for insulation, carpet backing etc. Sperling et al. [8, 9] have prepared soft rubbers from epoxidized oils cured with diacids and used the interpenetrating polymer networks to

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[a] Product names are necessary to report factually on available data; however the USDA neither guarantees nor warrants the standard of the product, and the use of the name USDA implies no approval of the product to the exclusion of others that may also be suitable.

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toughen polymers. Rösch et al. [10] prepared soft to rigid thermosets from epoxidized oils cured with different anhydrides. Liu et al. [11] have prepared soft to rigid composites of polyamine-cured epoxidized soybean oil with fillers and fibers. Shogren [12] has prepared citric acid-cured epoxidized soybean oil resins for use as coatings and showed that these disintegrate over time during soil burial.

There has been very little work published on the biodegradability of polymerized vegetable oil-based polymers. There have been reports of microbial deterioration of oil-based paints [13] and addition of fungicides to inhibit growth [14]. Erhan and Bagby [15] found that heat bodied (partially polymerized) soybean oil used in inks was nearly completely degraded to carbon dioxide and water. Many of the vegetable oil-based polymers described above are now used commercially or are in the process of commercialization so it would be desirable to understand the biodegradability of these systems. Such knowledge would be useful whether the polymer was intended to degrade safely in the environment or be durable and have long term resistance to degradation.

In this study, we have prepared a variety of vegetable oil-based polymers as shown in the reaction schemes of Fig. 1 and characterized the ability of soil microorganisms to mineralize these polymers into carbon dioxide and water.

EXPERIMENTAL

Materials

Refined food grade soybean oil and tung oil were from Alnoroil (Valley Stream, NY). Raw linseed oil was from Cargill (Wayzata, MN). Epoxidized soybean oil was Paraplex G-62 from C. P. Hall (Bedford Park, IL). Adipic acid, succinic acid, sebacic acid, citric acid, aluminum acetyl acetonate, tetrabutylammonium bromide and cobalt 2-ethylhexanoate solution in mineral spirits were from Aldrich (Milwaukee, WI). Brown kraft paper was nominal 40 lb. (per 3000 ft.^{2}) and was obtained from Carter Paper (Peoria, IL). Sand was Pak Mix play sand (Toledo, OH) and was dried at 120°C in an oven before use. Sources and grades of diglycidylether of bis-phenol A (DGEBA), triethyleneglycol diamine (TEGDA), triethylene tetramine (TETA), and diphenylmethane diisocyanate (MDI) are described in refs. 7, 11, and 16. Fumed silica, E-glass and Franklin fibers were used as specified in ref. 11. Appropriate safety precautions are needed in handling chemicals, especially MDI as they are toxic.

Preparation of Vegetable Oil-based Resins

Oxidatively polymerized oils were prepared by mixing native oils with cobalt 2-ethylhexanoate solution to give 0.02% Co, casting onto steel plates

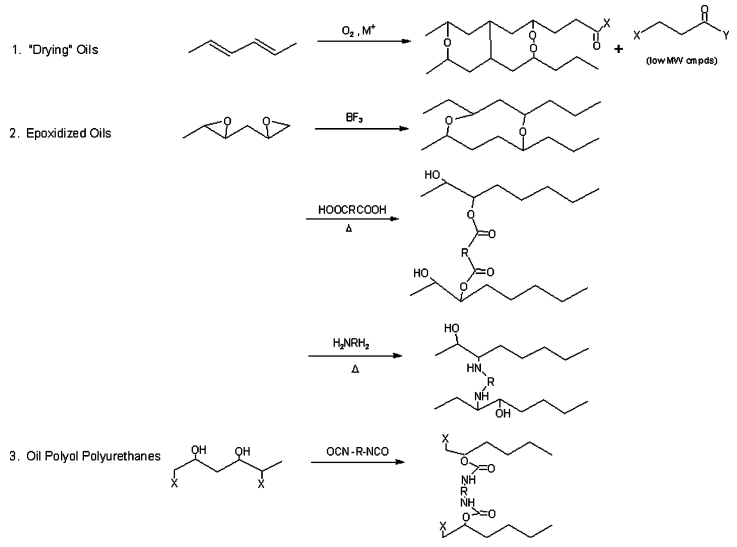

Fig. 1. Representative chemical structures of different types of cross-linking reactions. X and y may be any functional group, commonly H, OH, CH_3 or OCH_3.

and allowing air curing to proceed for 1 week. Samples were then pulverized by ball milling with stainless steel balls inside a steel vial cooled with liquid nitrogen (Brinkman, Des Plaines, IL). Sand (5 g/g sample) was added just after opening to help keep cured oil particles from fusing together into a solid mass as they warmed. Alternatively, oil and cobalt catalyst was coated onto kraft paper and allowed to cure in air for 1 week. FT-IR spectra of pulverized samples were obtained using a DuraScope single bounce diamond anvil (SensIR Technologies, Danbury, CT) mounted in an Impact 410 spectrometer (Nicolet Instruments, Madison, WI). Spectra were an average of 256 scans. The C–H stretching vibration adjacent to fatty acid double bonds (3010 cm^{-1}) was absent in the FT-IR spectra of all samples, suggesting that reactions were complete.

Epoxidized soybean oil (ESO)/dicarboxylic acid resins were prepared by heating ESO, acid (1 equivalent carboxylic acid/epoxy) and 1% aluminum acetyl acetonate or tetrabutyl ammonium bromide in a beaker with magnetic stirring at 180–190°C for 10 min. In the case of citric acid, water (6%) was added to aid dispersion of citric acid and heating temperature was 115°C. At this point, partially polymerized, homogeneous, slightly viscous solutions were obtained. Solutions were then poured onto polished steel plates and placed in an oven at 180°C (160°C for citric acid) for 30 min to complete polymerization. The soft rubbers obtained were pulverized and sand was added as described above. There was no noticeable epoxide ring vibration at 821 cm^{-1} in the FT-IR spectra of these resins, suggesting that most all of the ESO epoxy groups reacted.

Curing of ESO and blends of ESO and DGEBA with polyfunctional amines was carried out according to Liu et al. [11]. Briefly, ESO and blends were mixed with TEGDA or TETA and cured at 100°C for 24 h and then 150°C for 48 h. Some formulations also contained various amounts of DGEBA, fumed silica, calcium sulfate microfiber or E-glass fiber. Cured resins were cryogenically ground to a powder.

Polyurethanes from vegetable oil polyols and MDI were prepared according to Petrovic et al. [7, 16]. Polyols were prepared by epoxidation of the native oil followed by opening of the oxirane ring with methanol [6] or hydroformylation followed by reduction [17]. Note that the former method gives secondary hydroxyl groups while the latter gives primary hydroxyls. Polyols were preheated to 60°C, mixed with MDI and 0.2% catalyst (Cocure55, CasChem) and poured into a mould. Curing was carried out at 60°C for 1–2 h and 110°C overnight. Cured polyurethanes were cryogenically ground to a powder.

Respirometry

Respirometry was carried out using a Columbus Instruments 20 sample chamber Micro-Oxymax (Columbus, OH) equipped to measure CO_2 production and O_2 consumption and with condensing air driers. Samples (1.0 g, not including sand) were mixed with 50 g topsoil (Bluestem Solid Waste Agency, Cedar Rapids, IA) in 250 ml glass bottles and moisture was adjusted to 50% by weight. Topsoil was a fully composted mixture of leaves, grasses, wood, grain, sand and topsoil and had values of N_2, P_2O_5 and K_2O of 0.9, 0 and 0.35% and a pH of 6.1. Bottles were immersed in a water bath controlled at the desired temperature (30–58°C). Carbon dioxide levels were measured automatically every 2.5 h and bottles were flushed with fresh room air when CO_2 levels reached 0.5%. Either 2 or 3 replicates of each sample were measured. Moisture contents of the samples at the end of the experiment were typically 40%–45%. Theoretical yields of CO_2 were calculated from the carbon content of the samples. These respirometry methods are similar to those developed earlier by Imam and Gordon [18] and the ISO 17556:2003/ASTM D5988-03 standard methods.

RESULTS AND DISCUSSION

Simplified chemical structures of the products of the different polymerization reactions are shown in Fig. 1. These all result in the formation of three-dimensional networks although some low molecular weight ketones, carboxylic acids, and alcohols are formed in the oxidative polymerization via decomposition of oil hydroperoxides [1]. Functionality will increase in the order soybean, linseed and tung oil since these contain on average 4.5, 7.0 and 8.0 double bonds (or epoxy groups for epoxidized oils)/triglyceride molecule, respectively (Table I) [19].

Respirometry data for kraft paper coated with polymerized oils is shown in Fig. 2. The paper was used here as a biodegradable support since the polymerized oils are soft and sticky in some cases making thin film handling difficult. Paper coated with oxidatively polymerized soybean and linseed oil was 90%–100% converted to CO_2 after 65 days in soil at 30°C. Since these composites contained 50% oil, the

Table I. Fatty Acid Composition of Vegetable Oils Used for Polymerization Studies

	Avg. no. of fatty acids/triglyceride (d.b./TG)[1]		
Fatty Acid (d.b. position)	Soybean	Linseed	Tung
Palmitic C12:0	0.26	0.20	0.13
Stearic C18:0	0.18	0.12	0.03
Oleic C18:1 (9)	0.83 (0.8)	0.59 (1.2)	0.15 (0.2)
Linoleic C18:2 (9,12)	1.5 (3.0)	0.59 (1.2)	0.3 (0.6)
Linolenic C18:3 (9,12,15)	0.24 (0.7)	1.6 (4.8)	0
Eleostearic C18:3 (9,11,13)	0	0	2.4 (7.2)
Totals	3 (4.5)	3 (7.0)	3 (8.0)

[1]Average number of double bonds/triglyceride in parentheses.

extent of biodegradation of the polymerized oils must have been at least 80%–90%. The paper/ESO/citric acid composite degraded much more slowly, in agreement with previous weight loss data during soil burial [12, 20].

Mineralization data for polymerized vegetable oils which were cryogenically pulverized into a powder and absorbed onto sand are shown in Fig. 3. Biodegradation rates for oxidatively polymerized tung oil were much slower than for polymerized soybean or linseed oil. Tung oil has more double bonds per triglyceride and also has a high content of eleostearic acid. The latter has a conjugated system of double bonds at carbons 9, 11 and 13 and thus the resulting radicals would tend to be more stable and thus more likely to polymerize. It is likely that polymerized tung oil has a higher crosslinking density than soy or linseed oils and that these crosslinks inhibit the ability of esterases and other enzymes to

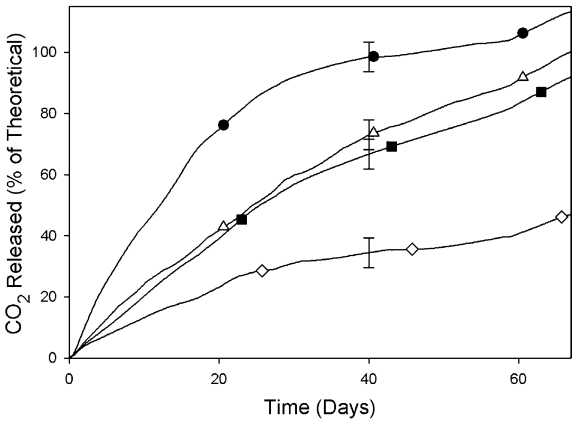

Fig. 2. Respirometry of kraft paper coated with oxidatively polymerized soybean oil (■), polymerized linseed oil (△), ESO/citric acid resin (◇) and uncoated paper control (●) at 30°C.

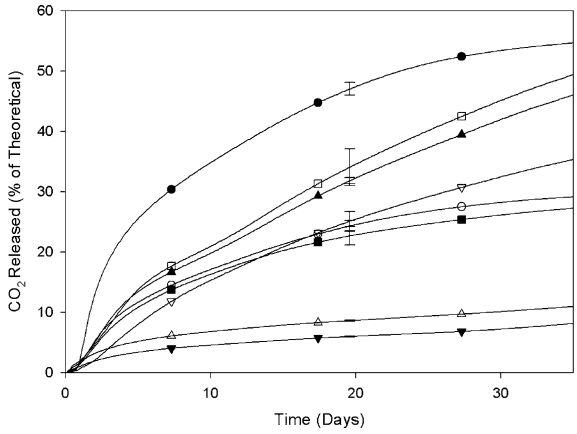

Fig. 3. Respirometry of oxidatively polymerized soybean oil (■), polymerized linseed oil (°), polymerized tung oil (⅄), ESO/succinic acid resin (□), ESO/adipic acid resin (⅄), ESO/sebacic acid resin (▽), ESO/citric acid resin (△), and neat ESO control (●) at 30°C.

bind to and degrade the oil network. The relatively rapid biodegradation rates for polymerized soybean and linseed oils is somewhat surprising given the non-degradable nature of the carbon–carbon and carbon–oxygen cross-links (Fig. 1). Enhanced rates of biodegradation may be due to the presence of oxidized chain ends such as carboxylic acids within the network which may be more readily degraded by microbial enzymes.

Epoxy resins made from ESO and aliphatic dicarboxylic acids such as succinic, adipic and sebacic were found to be mineralized rather quickly in soil at 30°C (Fig. 3). The ester crosslinks formed in these systems are probably sensitive to hydrolysis perhaps by esterases or even water alone. (It was observed that some of these materials became softer after exposure to humid room air for >1 year.) Epoxy polyesters cured with glutaric anhydride were found to hydrolytically degrade over a period of 10 weeks in phosphate buffer of pH 7.4 at 70°C [21]. Mang et al. also found that polyesters derived from diacids and diglycidyl ethers were biodegradable in soil [22]. Biodegradation rates of the ESO/citric acid resin were much slower than the resins made with the dicarboxylic acids. With three carboxylic acid groups on adjacent carbons, accessibility of enzymes to the ester groups in the ESO/citric acid resin would be expected to be diminished by steric effects or higher cross-link density.

Carbon dioxide production from amine-cured epoxy resins and soybean oil control samples in soil at 58°C are presented in Fig. 4. After 100 days, the soybean oil was 97% converted to CO_2 and water.

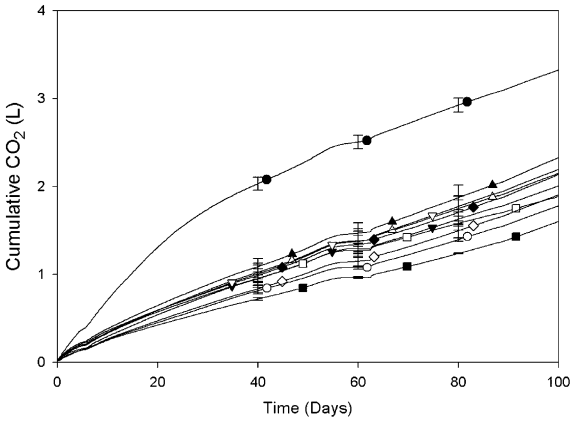

Fig. 4. Respirometry of amine-cured epoxy resins at 58°C: ESO/TEGDA (⅄), ESO/TEGDA/FS6.9/FF22 (♦), ESO/TEGDA/FS5.2/EG41 (⅄), ESO/TETA (△), ESO/TETA/FS4.4/EG51 (◇), ESO/DGEBA/TETA/FS5.9/FF22 (∇), ESO/DGEBA/TETA/FS5.9/FF22 (■), ESO/DGEBA/TETA/FS3.0/EG60 (°), soybean oil control (●) and soil only (□). The letters FS, FF and EG refer to fumed silica, Franklin fiber H-45 and E-glass fiber, respectively; numbers following these abbreviations represent weight percentage of ingredient.

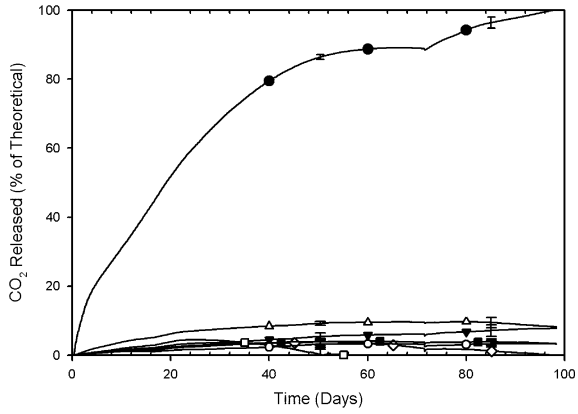

Fig. 5. Respirometry of vegetable oil-based polyurethanes made from following polyols: triolein-met (⅄), soy-HF (■), soy-met 180 (◇), soy-met 206 (°) and linseed-met (□). Also shown is ESO/BF_3 polymer (△) and soybean oil control (●). Temperature was increased from 30°C to 55°C on day 71. Note hydroxyl number of 180 is the functionality of 3.3; 206 is 4.0. Met refers to polyol made from ESO and methanol; HF refers to polyol from hydroformylated and reduced ESO.

Carbon dioxide production for the epoxy resins were, however, not significantly different from the control soil alone. This was the case irrespective of the type of amine (triethyleneglycol diamine or triethylene tetramine), whether DGEBA was added to ESO, or if mineral fillers and fibers were added up to 65%. Polymers with amine type linkages in the backbone are not generally thought to be biodegradable [23]. This is consistent with our results which suggest that amine cross-links between fatty acid chains inhibit the biodegradation of triglyceride network polymers.

Respirometry data for vegetable oil polyurethanes and soybean oil control in soil at 30°C (days 1–70) and 55°C (days 71–98) are shown in Fig. 5. Mineralization of soybean oil to CO_2 was complete (100%) by the end of the experiment. There was very little (0%–7.5%) of the carbon in the polyurethanes that was converted to CO_2 over the course of the experiment. It appeared that, for most of the samples, that CO_2 released increased near the beginning of the experiment then remained constant with time. This suggests that there may be a small fraction of the polyurethanes, such as a lower molecular weight fraction, that degrades quickly leaving the bulk recalcitrant higher molecular weight material. There also appeared to be a trend toward less degradation as the polyol functionality increased (linseed < soy < triolein) but the differences were similar to error levels so they may not be significant. Although some polyurethanes are known to be biodegradable, particularly those with polyester soft segments, generally the aromatic urethanes are slow to degrade [23].

Data in Fig. 5 also show that ESO crosslinked by cationic ring opening with BF_3 is very slow to biodegrade. The ether crosslinks formed in this reaction are probably difficult for biological systems to break down as most high molecular weight polyethers are known to degrade very slowly [24].

CONCLUSIONS

In summary, it appears that cross-linking triglycerides with non-degradable linkages results in loss of biodegradability. The presence of cross-links or branches in the fatty acid portion of the triglyceride network probably inhibits binding and activity of lipases which cleave the glycerol ester bonds. Alternatively, some glycerol ester bonds might be cleaved but further metabolism of the fatty acids would be blocked by the branch points. The relatively rapid biodegradation of oxidatively polymerized soybean and linseed oils suggests that there are likely parts of the network which contain chain ends having groups susceptible to biodegradation such as carboxylic acid or alcohols. The cross-linking density of these networks is also likely lower than the other systems due to the formation of oxidized species in addition to radical combination and cross-linking. Triglyceride networks containing hydrolysable ester bonds, especially linear diesters, are biodegraded

fairly rapidly in soil. More branched polyester cross-links such as those formed by citric acid are degraded more slowly probably as a result of steric interference of enzyme accessibility. This study has examined rates of biodegradation in soil only. Different microbial populations and physical conditions are present in different environments such as activated wastewater treatment sludge, composting centers, rivers, oceans [25]. Different rates of biodegradation would be expected for polymerized vegetable oils in these different environments though similar trends might be expected among the different samples examined here.

ACKNOWLEDGMENTS

The authors would like to thank Elizabeth Krietemeyer for performing the respirometry experiments, John Salch for the FTIR work and Dr. Syed Imam for valuable help in developing some of the respirometer methodology.

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